

Segregation in aqueous methanol enhanced by cooling and compression

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Molecular segregation in methanol-water mixtures is studied across a wide concentration range as a function of temperature and pressure. Cluster distributions obtained from both neutron diffraction and molecular dynamics simulations point to significantly enhanced segregation as the mixtures are cooled or compressed. This evolution toward greater molecular heterogeneity in the mixture accounts for the observed changes in the water-water radial distribution function and there are indications also of a change in the topology of the water clusters. The observed behavior is consistent with an approach to an upper critical solution point. Such a point would appear to be "hidden" below the freezing line, thereby precluding observation of the two-fluid region.

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I. INTRODUCTION

Amphiphiles are a particularly important class of molecule containing both hydrophobic and hydrophilic domains with competing solubility properties. Association of non-polar moieties leads to the formation of micelles and other modulated structures. Due to the local density variations inherent to many self-assembled amphiphilic structures, simple equations of state fail to give a complete description of phase equilibria. The simplest amphiphiles (the primary alcohols such as methanol, ethanol and propanol) are widely studied and have been found to be completely miscible in all proportions and at all state points studied. Recently, however, experimental and computational studies on aqueous methanol have revealed unexpectedly complex behavior at medium lengthscales leading to a substantially revised view of miscibility in this prototype aqueous amphiphile[1, 2, 3]. In particular, molecular-level segregation has been observed with the alcohol agglomerates exhibiting structural details consistent with those expected for a hydrophobically-driven system[1, 3]. Moreover, percolating clusters have been found for both components in a certain concentration range over which many thermodynamic functions and transport properties reach extremal values [4].

Despite the intense activity and success in studying these model systems at room temperature and pressure, there have been no systematic investigations aimed at mapping out the behavior of these observed extended structures under non-ambient conditions. Even in systems which exhibit clear miscibility gaps, the pressure dependence of the critical solution temperature can increase, decrease or remain constant[5] and little information exists on molecular-level structure. Such measurements on the model methanol-water mixture are needed

to develop and refine molecular-level models of the entropic and enthalpic factors governing the phase behavior of aqueous amphiphiles. These models are potentially of wider significance to areas such as membrane and protein stability.

Partial miscibility is a common feature of binary liquid phase equilibria in which a mixture separates into two phases of different compositions[5] depending on temperature and pressure. This behavior follows directly from the *Gibbs phase rule* and is contained within simple molecular thermodynamic models such as Bragg-Williams theory. Typically, an immiscible region terminates at an *upper critical solution temperature* (UCST), above which the mixture is fully miscible. In some hydrogen-bonded systems, however, further cooling leads to re-entrant miscibility and a closed-loop gap in the phase diagram appears[6, 7, 8]. We therefore report here an attempt to explore structural properties of methanol-water mixtures far from the ambient state point. We use a combination of neutron diffraction with comprehensive isotope substitution and classical molecular dynamics simulations. The specific objective of the work is to identify the separate effects of temperature and pressure on the structures formed in these solutions, the combined effects of temperature and pressure and to comment on the nature of intermolecular contacts in these solutions.

II. EXPERIMENTAL AND SIMULATION DETAILS

Protiated and deuteriated samples of methanol and water were obtained from Sigma-Aldrich and used without additional purification. Neutron diffraction measurements were performed on the SANDALS time-of-flight diffractometer at the ISIS pulsed neutron facility at the Rutherford Appleton Laboratory in the UK. The liquid

samples were contained in flat plate cells constructed from a Ti-Zr alloy from which coherent scattering is negligible. These were mounted on a closed cycle refrigerator, and neutron diffraction measurements were made at a number of different temperatures and pressures (Table I). For the high pressure experiments, the sample was contained in several 1.5 mm cylindrical channels cut into a flat TiZr plate. Pressure was applied using an intensifier. The high pressure experimental arrangement has been described in detail in a previous publication [9]. The data were corrected for attenuation, inelastic and multiple scattering using the ATLAS programme suite [10]. The differential scattering cross-section for each sample was obtained by normalising to a vanadium standard sample. A total of 7 isotopically distinct samples were measured for methanol mole fractions $x = 0.27$, $x = 0.54$ and $x = 0.70$. These were respectively (i) CD_3OD in D_2O ; (ii) CD_3OH in H_2O ; (iii) a 50:50 mixture of (i) and (ii); (iv) CH_3OD in D_2O ; (v) a 50:50 mixture of (i) and (iv); (vi) CH_3OH in H_2O ; and (vii) a 50:50 mixture of (i) and (vi). For $x = 0.05$, 5 samples were measured, namely (i), (ii), (iii), (vi) and (vii) and for $x = 0.50$ (i), (ii), (iii), (iv) and (v). These procedures lead to a structure factor $F(Q)$ having the form $F(S_{HH}(Q), S_{XH}(Q), S_{XX}(Q))$ where $S_{HH}(Q)$ relates to correlations between labelled atoms and $S_{XH}(Q)$ and $S_{XX}(Q)$ are the two composite partial structure factors which give the remaining correlations between other types of atoms (X) and the labelled atom type (H) in the form of a weighted sum of individual site-site partial structure factors.

Diffraction data is analyzed using the Empirical Potential Structure Refinement procedure (EPSR) [11]. According to this method, a three-dimensional computer model of the solution is constructed and equilibrated using interaction potentials taken from the literature. The charges and Lennard-Jones constants from the SPC/E potential of Berendsen et al [12] were used for the water molecules. The H1 potential of Haughney et al [13] was used for the methanol molecules. Methanol-water interactions were simulated by Lorentz-Berthelot mixing rules [14]. Information from the diffraction data is then introduced as a constraint whereby the difference between observed and calculated partial structure factors enters as a potential of mean force to drive the computer model (via Monte Carlo updates of atomic positions) toward agreement with the measured data. This procedure results in an ensemble of three-dimensional molecular configurations of the mixture exhibiting average structural correlations that are consistent with the available diffraction data. A total of 600 molecules (methanol and water) are contained in a cubic box of the appropriate dimension to give the measured density of each solution at the appropriate temperature (Table I). Periodic boundary conditions are imposed. A comparison between the experimentally-measured partial structure factors and those generated from the ensemble-averaged EPSR with 10000 configurations is shown in Fig 1.

We have performed a series of classical molecular dy-

Mole fraction x	Temp. $/K$	Pressure kbar	Total No. molecules	No. of methanol molecules	No. of water molecules
0.27	293	amb	600	162	438
0.27	238	amb	600	162	438
0.50	200	amb	600	300	300
0.50	200	2.0	600	300	300
0.54	298	amb	600	324	276
0.54	260	amb	600	324	276
0.54	190	amb	600	324	276
0.70	293	amb	600	420	180

TABLE I: Parameters of the methanol-water mixtures used in the Empirical Potential Structural Refinement.

Mole fraction x	Temp. $/K$	Pressure kbar	Total No. molecules	No. of methanol molecules	No. of water molecules
0.27	298	amb	600	162	438
0.27	298	2.0	600	162	438
0.50	200	amb	600	300	300
0.50	200	2.0	600	300	300
0.50	298	2.0	600	300	300
0.54	298	amb	600	324	276
0.54	190	amb	600	324	276
0.70	298	amb	424	297	127
0.70	298	2.0	424	297	127

TABLE II: Parameters of the methanol-water mixtures used in the Molecular Dynamics simulations using **DL_POLY**.

namics simulations using the **DL_POLY** code [15] employing previously tested intermolecular potentials for both methanol [16] and water [17]. Both molecular species are modelled using a fully-flexible, all-atom approach with specific van der Waals terms for each atom type. Our previous studies [4], [18] have shown this code and these potentials can predict the local and extended structural and dynamical behaviour of these mixtures across the composition range in close agreement with empirical observation. The simulations were run to produce 2ns trajectories using 0.5fs timestep with an equilibration time of over 0.5ns. The sampling interval on the trajectories were every 0.1ps. Due to this wealth of data, most of the subsequent statistical analysis was done only on the second half of the trajectory giving around 10000 data points. Details of systems used in simulations are given in Table II.

Temporal averages of the molecular dynamics simulations and configurational averages of the EPSR-generated ensembles were then interrogated to extract complete sets of intermolecular structural correlations including information on short-range (solvation) and medium-range (clustering) structure. In the case of water, clusters are defined by those molecules that participate in a continuous hydrogen-bonded network. Two water molecules are considered to be hydrogen-bonded if the inter-oxygen contact distance is less than approximately 3.5 Å, the radial distance of the first minimum of

the $g_{Ow-Ow}(r)$ pair correlation function for both EPSR and MD ensembles. The definition of a cluster is ambiguous in the case of methanol and can be made two different ways. The first is on the basis of hydrogen-bond connectivity, i.e. if constituent methanol oxygen atoms are less the distance of the first minimum in the $g_{O-O}(r)$ pair correlation function. The second is through methyl group association, where two methanol molecules are assigned to the same cluster if the C-C distance is less than the minimum following the first peak determined from the $g_{C-C}(r)$ pair correlation function (which is approximately 5.7 Å). The former is more common in pure methanol whereas the latter connectivity type is believed to be characteristic of molecular association that is driven by the hydrophobic interaction. These two types of clusters are subsequently referred to as polar contact clusters and non-polar contact clusters.

III. RESULTS

A. Cluster distributions at low temperature

We have already demonstrated in a previous publication[4] that the methanol-water system exhibits significant micro-segregation across a wide range of compositions, forming localised pockets of a single species of varying size and topology. These clusters are characterised according to the criteria outlined previously. The behavior of water cluster distributions on cooling at mole fraction $x = 0.54$ are shown in Fig 2. The number of clusters containing i molecules is plotted as a fraction of total number of clusters, $M(i)/M$ (where $M = \sum_i M(i)$) against the cluster size i . The cluster distributions show an enhanced probability of the largest clusters on cooling, at the expense of medium-sized (100 molecules or so) clusters. There are slight differences in the experimental and simulation-derived distributions plots; the depleted region of medium-sized clusters in the MD simulations is wider and the enhanced peak of the largest clusters is narrower than the corresponding features in the experimental plot. However, the plots do show the same trends, with the main features being that the system exhibits larger water clusters and these clusters are more frequently present upon cooling. This is consistent with increased segregation of the two components upon cooling. The same trends are seen in the EPSR analysis of a mole fraction $x = 0.27$ mixture, although the effect is less marked since the water clusters are already bigger at this concentration. Results of MD simulations at other compositions (not shown) show the same behaviour in water cluster size distribution on cooling.

B. Cluster distributions at elevated pressure

The effect of compression to 2kbar on the ambient temperature methanol-water cluster distributions deter-

mined by analysis of MD simulations is shown in Fig. 3 at several concentrations, $x = 0.70$, $x = 0.54$ and $x = 0.27$. Also shown is the predicted power law $n_s \approx s^{-2.2}$ for random percolation on a 3-d cubic lattice[19]. The results for water clusters in the system and the effect of increased pressure is most evident on the solutions of methanol mole fraction $x = 0.7$ and $x = 0.54$. In both cases, the size and probability of occurrence of the largest water clusters is increased. Particularly striking is the case of the most concentrated ($x = 0.7$) mixture where compression of 2kbar changes the water connectivity from isolated non-spanning clusters to a percolating network. The effect on the most dilute solution ($x = 0.27$) is less obvious as the ambient pressure results indicate that this solution already comprises very large water clusters, in excess of the theoretical limit for random percolation. We thus find that the effect of pressure is also to enhance segregation at all concentrations studied. The qualitative effect of compression is therefore very surprising, being the same as the effect of cooling. This result is unexpected and contradictory to the general expectation that compression should have had the opposite, deconstructing effect. The methanol cluster distributions, both non-polar and polar (as defined previously) were also explored. In the case of the non-polar clusters, it is difficult to discern a notable effect of compression: the cluster distributions of even the ambient pressure systems are dominated by large clusters, often comprising all the methanol in the system. Likewise for the polar clusters, of which there are only a relatively small number of small clusters, the effect of compression is rather small.

C. Cluster distributions at elevated pressure and reduced temperature

We also consider the effect of compressing the cooled system. Figure 4 shows the corresponding results for water clusters from EPSR analysis of the neutron data and MD simulations obtained at $x = 0.50$ and $T=200K$ at ambient pressure and 2kbar. The effect of compressing a cooled system appears to be a further enhanced probability of larger water clusters, as was seen previously for the effects of lowered temperature or compression alone. The effect is clearest from the EPSR analysis, where once again the depletion of medium size water clusters is evident. The cluster distribution shows an enhanced probability of the largest clusters on compression, at the expense of these medium-sized clusters. The data from the MD simulations are broadly consistent with this picture, and appear to show a bimodal distribution of large cluster sizes, centered around 250 and 280 water molecules. At this composition, there are only 300 water molecules in the system, indicating that these two peaks actually pertain to the same cluster, which absorbs or sheds smaller clusters during the course of the simulation. The prominent peak around a cluster size of 30 is a strong candidate for involvement in this process. We return to the differ-

ences between EPSR and MD data in the discussion.

D. Local structure

In this section we examine the local structure focussing on the pressure and temperature behavior of the water oxygen radial distribution function $g_{Ow-Ow}(r)$. We first consider the effects of concentration on this RDF at ambient temperature and pressure. Fig 5 shows data from both EPSR and MD analyses. Even at the lowest concentration, with mole fraction $x = 0.27$ we find that a perturbation to $g_{Ow-Ow}(r)$ compared to that of pure water is evident. The location of the second maximum shifts $\approx 0.2\text{\AA}$ to higher r from the MD simulations. At increasing concentrations we find, for both experiment and MD simulation, progressively larger shifts in the 2nd peak position to larger r values. This shift to higher r implies that the water clusters are becoming less like bulk water, which is supported by cluster distribution[4], which show smaller average water cluster sizes with increasing methanol concentration. We assume this is a consequence of the water being confined to increasingly smaller domains by the surrounding methanol hydroxyl groups and consequent interfacial tension.

The effect of cooling on $g_{Ow-Ow}(r)$ is also shown in Figure 6. At $x = 0.27$ (not shown) we find that the main features of the distribution are sharpened perhaps indicative of reduced dynamic disorder but that there are no other significant changes. By contrast, at the higher alcohol concentration of $x = 0.54$, comparatively large structural perturbations induced by the presence of the alcohol molecules are partially reversed on cooling and the displaced second shell peak in the radial distribution function moves back towards its original position (i.e. that of pure water). As the position of this 2nd peak is generally associated with tetrahedrality of the local water structure, both the EPSR analysis of the experimental data and the MD simulations suggest that the previously perturbed tetrahedral structure of the water is recovered on cooling.

We next consider the effect of compression on the local structure at ambient temperature. MD simulations of a $x = 0.54$ mole fraction solution do not show any obvious change to the position of the second peak in the $g_{Ow-Ow}(r)$ (in contrast to the data in Fig 6 for low temperature). Interestingly, it is the methanol $g_{C-C}(r)$ radial distribution function which is perturbed most significantly, and this is shown in Fig 7. At three different concentrations $x=0.70$, $x=0.54$ and $x=0.27$, the first and second peaks in $g_{C-C}(r)$ are seen to shift to lower r values. This shift is approximately the same for all concentrations as the methanol content is increased. This indicates that the methyl groups are squeezed together as the pressure is increased. It appears that it is the methanol which is most responsive to the pressure.

Finally we consider the combined effect of reduced tem-

perature and elevated pressure on the local structure. We might have expected the combined effect to be similar to the sum of the effects of the constituent parts. However, from both EPSR analysis and MD simulations we find (see Fig. 8) that compression of a cooled solution results in a further shift to lower r of the second peak in the $g_{Ow-Ow}(r)$. Thus the water appears to partially recover its unperturbed (ie ambient pressure and temperature) structure. In addition, the first and second peaks in the methanol $g_{C-C}(r)$ are shifted to lower r , analogous with the situation for the compression of the solution at ambient temperature.

IV. DISCUSSION

The prediction from both the EPSR analysis and MD simulations is one of enhanced segregation of methanol and water on cooling, evidenced by the more frequent existence of larger water clusters, in comparison to room temperature data. This is the kind of behaviour we would expect on a microscopic scale if the system were moving towards a phase boundary, characterised by an upper critical solution temperature. Such immiscibility has not been observed in the methanol-water system, this is because the intervening solid phase precludes access to any possible two-fluid region in methanol-water mixtures. The clustering behaviour at low temperature provides a consistent framework within which to interpret the observed variations in local structure, particularly $g_{Ow-Ow}(r)$. As the temperature is lowered the formation of larger clusters leads to increased connectivity of the water domains. Within these growing water clusters the local structure evolves toward that of bulk water. The effect is most obvious with the methanol-rich solutions studied, of mole fraction $x = 0.54$.

Compression of the solution leads to the same effect on the medium-range order of the system, that is to enhance segregation by formation of larger water clusters. However, the local structure shows little if any change in the positions of the peaks in $g_{Ow-Ow}(r)$. In contrast, the corresponding RDF for methanol carbon atoms in systems at elevated pressure is displaced to lower r at all concentrations. It would seem therefore that the topology of the larger clusters formed by enhanced pressure is different to those formed by lowered temperature, since the water contained within them does not show a significant trend in the RDF back towards that of bulk water (as was the case for lowered temperature).

Both the MD simulations and the EPSR analysis predict qualitatively the same trends of enhanced clustering as a function of lowered temperature and increased pressure. There are however differences in the predicted cluster distributions. One possible reason for this may be the sampling of different average configurations. The EPSR analysis samples Monte Carlo configurations, whereas the MD samples temporal snapshots. Within the cluster analysis of MD simulations, a peak in the cluster

distribution plots may occur from either a large number of clusters of size i occurring or a relatively smaller number of the same size that persist for a long period of time during the simulation. It is not surprising therefore that the precise details of the cluster distributions are different since they represent different methodologies of arriving at the same prediction. The qualitative trends are clear from both analyses; that clustering, and hence segregation of the two species, is enhanced by elevated pressure or reduced temperature. A clear example of the differences in distributions is shown in Figure 4, for the compression of a low temperature $x=0.54$ mole fraction solution. The EPSR analysis clearly shows that the size of the largest water cluster increases and clusters of that size are more frequently found compared to the ambient pressure case. The MD results on the other hand are indicative of larger clusters in the sense that they predict the existence of two very large clusters (though not simultaneously) centered around 250 and 280 molecules. The combined probability of these clusters is greater than that of the largest clusters present in the ambient pressure data.

We note that our results concerning the enhanced segregation at elevated pressure are in contrast to the results of Hummer *et al* [20] who have concluded that pressure destabilises the contact configuration of non-polar molecular groups, relative to a solvent-separated configuration. These authors then assert that pressure denaturation of proteins proceeds by a similar mechanism, that is solvent penetration into a hydrophobic core. In contrast to this our results from diffraction measurements and simulations indicate the hydrophobic groups get pushed closer together with pressure. This difference may be due to the consequence of having an amphiphile in solution rather than a simple hydrophobe.

V. CONCLUSION

A series of methanol-water solutions have been investigated by neutron diffraction and MD simulation over a range of concentrations, temperatures and pressures. The diffraction data were analysed using the EPSR technique which was found to give results qualitatively similar to that from MD simulations, although there are some

differences in detail. A general conclusion of these studies is that lowering the temperature has the effect of enhancing the degree of microsegregation between methanol and water that occurs in these systems.

More surprisingly, increasing the pressure appears to have the same effect, which argues against the notion that pressure denaturation of proteins is caused by water entering the hydrophobic core of a protein: if it did so we might have expected to see a decrease in the clustering with increased pressure, not increased clustering. The second shell of water g_{Ow-Ow} appears to expand slightly with increasing methanol concentration, suggesting a general opening up of the water structure as the water concentration diminishes: this effect is to be analysed to identify whether it is primarily a surface effect or proceeds throughout the water. This expansion is if anything reversed on lowering the temperature or increasing the pressure. We speculate that these trends could be an indication of the approach to an upper critical solution boundary, which however is not observed due to the intervening solid phases.

Overall the methanol-water system has proved itself to be a rich source of phenomena which may be of relevance to situations involving much larger and more complicated molecules. Methanol and water are ideally suited to the experimental diffraction and atomistic simulation methodologies due to their simple molecular forms, and their ready availability in different isotopic forms. Yet this simple model system can apparently capture much of the essence of hydrophobicity in aqueous systems in a way that it might occur in the much larger molecular entities, with mixed hydrophobic and hydrophilic head-groups of real biological systems. The present results should therefore help guide the search for possible mechanisms which control molecular conformation in aqueous solution.

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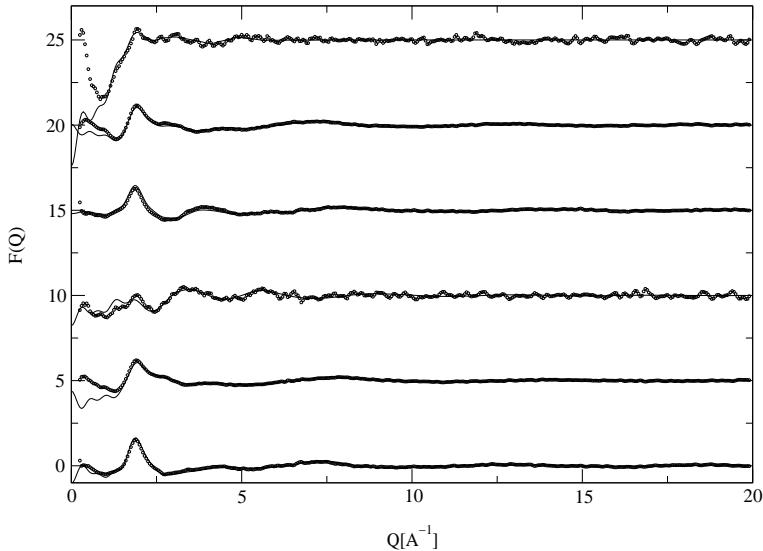


FIG. 1: Typical example of the fits (lines) obtained by the EPSR analysis compared to the original data (circles). The data shown in this case ($x = 0.50$ at 200K and 2kbar) are the interference differential scattering cross-sections for the samples (i) through (vi) described under Methods. Discrepancies are observed in the low Q region. These are caused by difficulties in removing completely the effect of nuclear recoil from the measured data. However this recoil effect is expected to have only a monotonic dependence on Q and so is unlikely to influence the model structure to any significant extent.

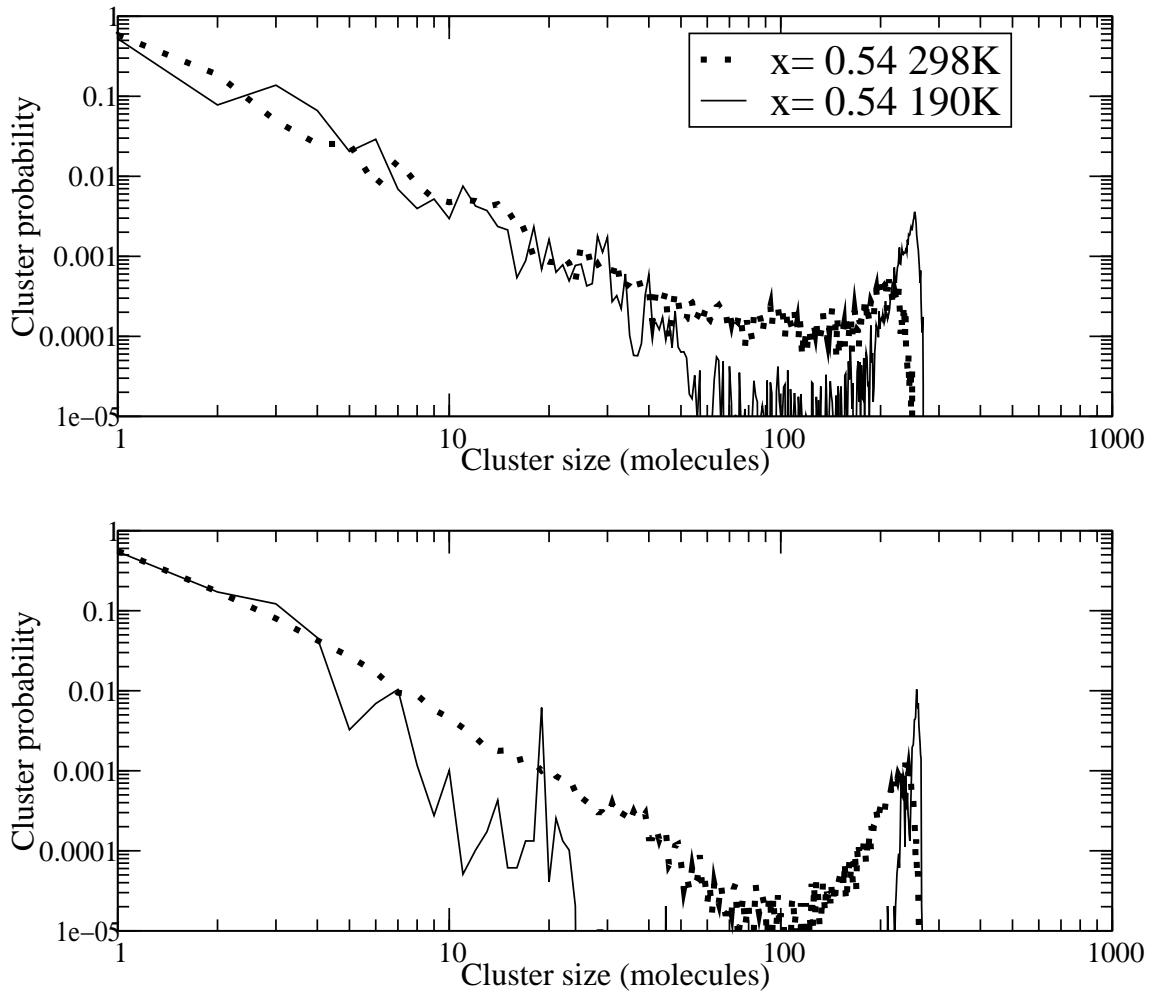


FIG. 2: The effect of cooling on water cluster distributions for $x=0.54$ from EPSR analysis (top) and MD simulations (below)

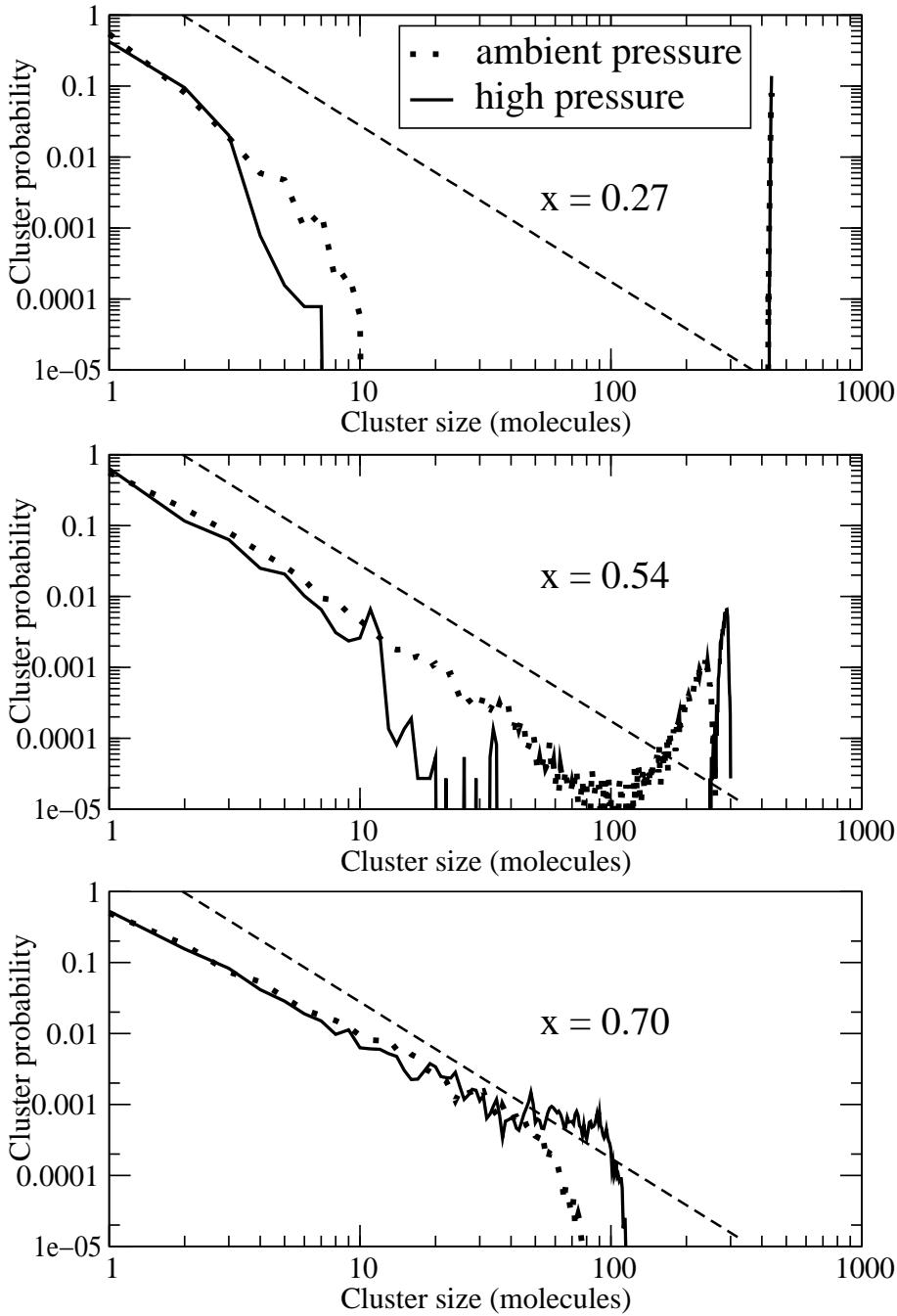


FIG. 3: The effect of compression on MD simulation cluster distributions for mole fraction $x = 0.27$ (top), $x = 0.54$ (middle) and $x = 0.70$ (bottom) for water clusters. Ambient conditions are shown as dotted lines and high pressure shown as solid lines. The predicted power law $n_s \approx s^{-2.2}$ for random percolation on a 3-d cubic lattice[19] is shown as a dashed line.

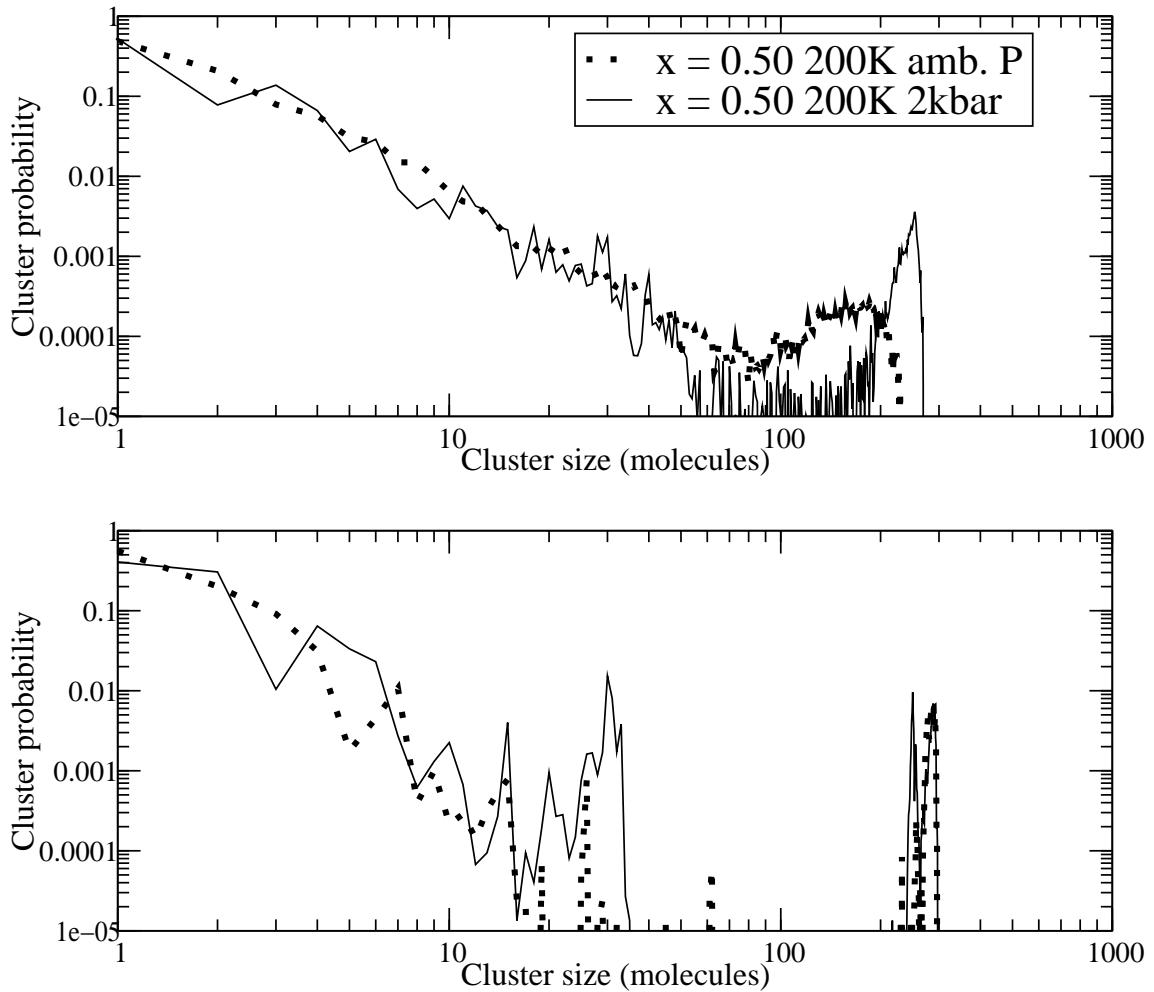


FIG. 4: The effect of compressing a cooled system for mole fraction $x = 0.50$ on water cluster distributions from EPSR analysis (top) and MD simulations (below)

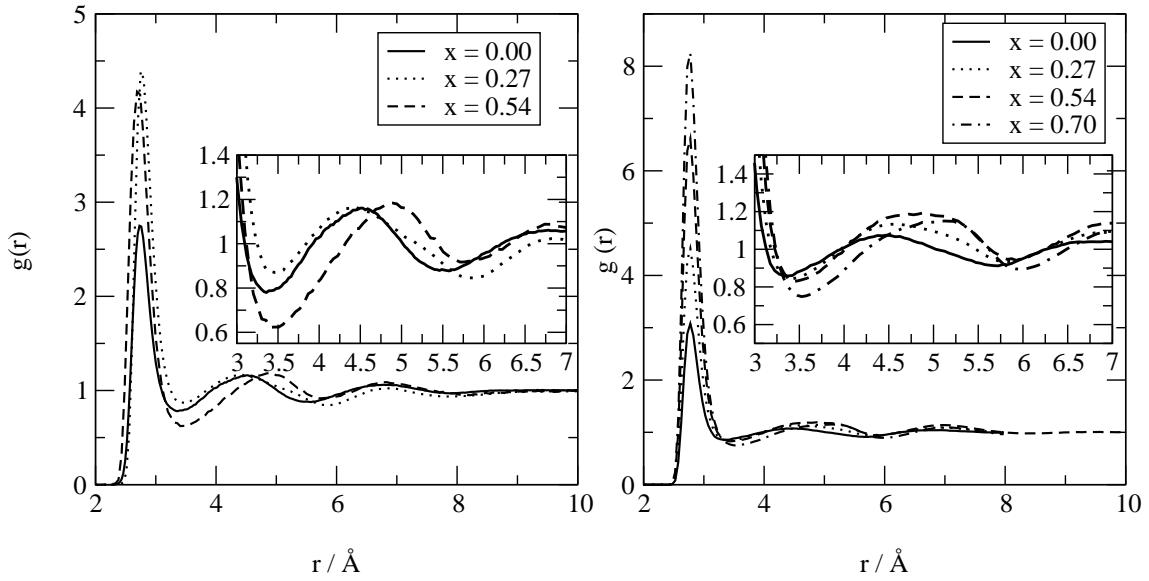


FIG. 5: Water radial distribution functions $g_{Ow-Ow}(r)$ from both EPSR analysis (left) and MD simulations (right) at different concentrations. Inset shows detail of second peak.

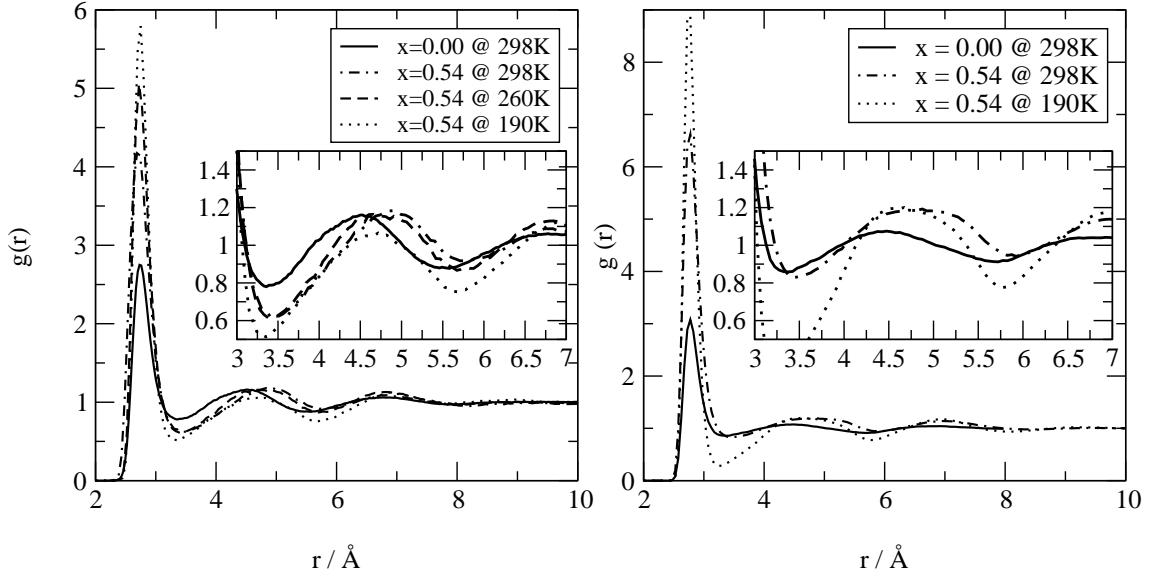


FIG. 6: The effect of cooling on the water radial distribution function $g_{Ow-Ow}(r)$ from both EPSR analysis (left; $x=0.54$ at 298K, 260K and 190K) and MD simulation (right; $x=0.54$ at 298K and 190K).

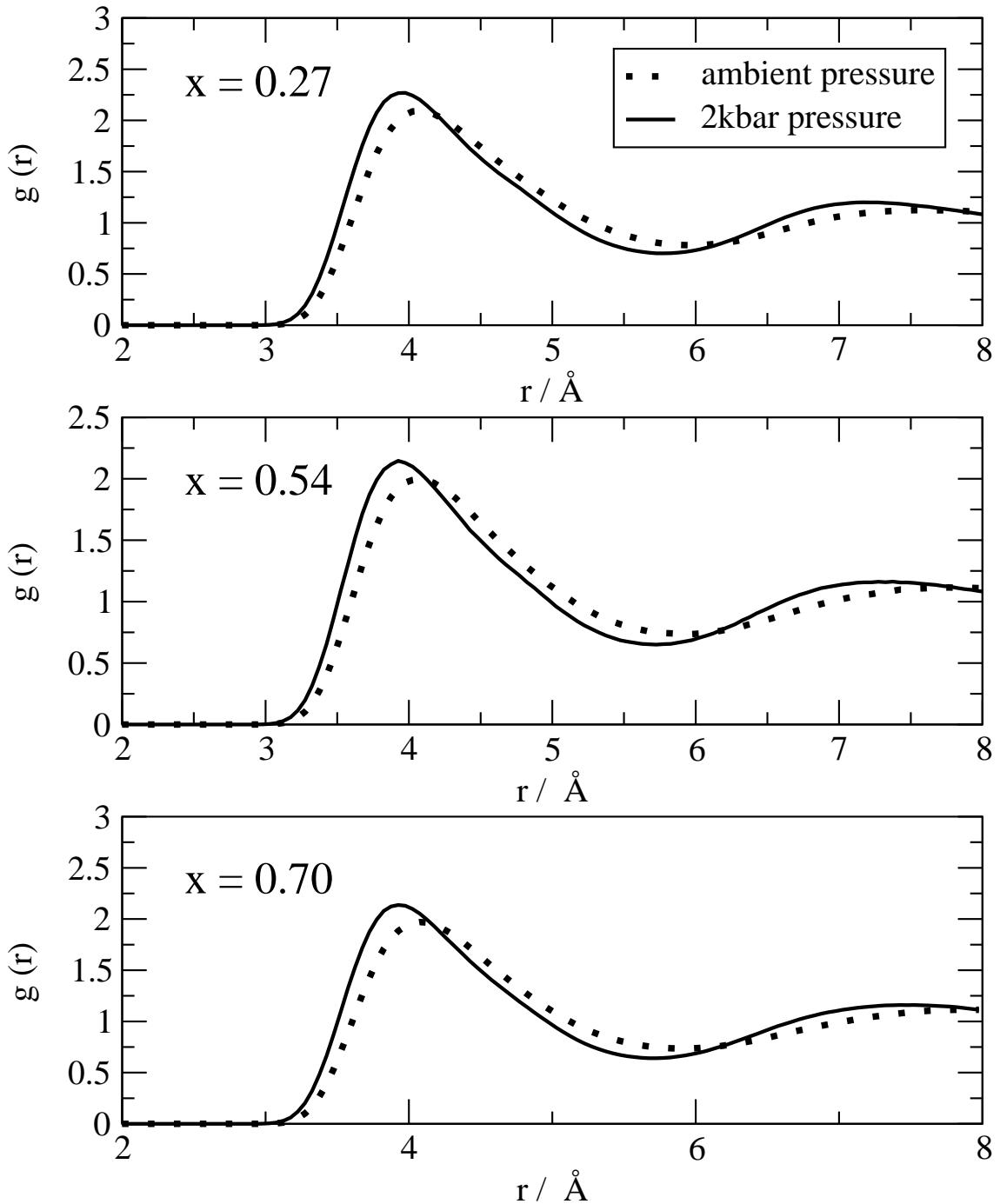


FIG. 7: Methanol $g_{C-C}(r)$ radial distribution functions from MD simulations (mole fraction $x=0.27$; 0.54 and 0.70).

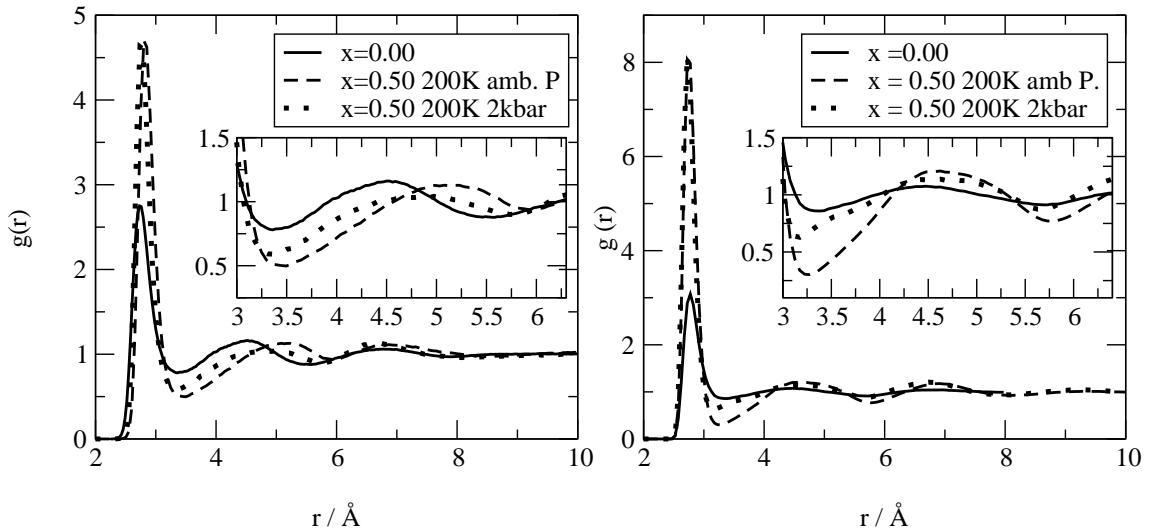


FIG. 8: Water radial distribution functions $g_{Ow-Ow}(r)$ for mole fraction $x=0.50$ at 200K, variable pressure from EPSR analysis (left) and MD simulations (right)